(54) Title: PROCESS FOR THE PRODUCTION OF ULTRAFINE PARTICLES

(57) Abstract

A new, cost effective process for the production of ultrafine particles which is based on mechanically activated chemical reaction of a metal compound with a suitable reagent. The process involves subjecting a mixture of a metal compound and a suitable reagent to mechanical activation to increase the chemical reactivity of the reactants and/or reaction kinetics such that a chemical reaction can occur which produces a solid nano-phase substance. Concomitantly, a by-product phase is also formed. This by-product phase is removed so that the solid nano-phase substance is left behind in the form of ultrafine particles. During mechanical activation a composite structure is formed which consists of an intimate mixture of nano-sized grains of the nano-phase substance and the reaction by-product phase. The step of removing the by-product phase, following mechanical activation, may involve subjecting the composite structure to a suitable solvent which dissolves the by-product phase, while not reacting with the solid nano-phase substance. The process according to the invention may be used to form ultrafine metal powders as well as ultrafine ceramic powders. Advantages of the process include a significant degree of control over the size and size distribution of the ultrafine particles, and over the nature of interfaces created between the solid nano-phase substance and the reaction by-product phase.

- 1 -

PROCESS FOR THE PRODUCTION OF ULTRAFINE PARTICLES

FIELD OF THE INVENTION

The present invention relates to a process for the production
of ultrafine particles and relates particularly, though not
5   exclusively, to the production of ultrafine metallic and non-
metallic powders consisting of individual particles with
sizes in the range of 1 nm to 200 nm.

BACKGROUND TO THE INVENTION

Ultrafine powders have significant potential for a wide range
10 of applications including catalysts, magnetic recording
media, optoelectronic materials, magnetic fluids and
composite materials. Ultrafine metallic powders have been
prepared by physical methods, such as vapour deposition and
sputtering, which have high quality, i.e. clean surfaces and
15 uniform particle size distribution. However, industrial
applications for such powders are limited by low yield rates
and high cost. Alternative chemical production methods, such
as thermal decomposition and precipitation are currently
being studied for the preparation of a wide range of powders.
20 Chemical methods can provide large quantities of ceramic
powders for industrial applications. However, except for
precious metals, chemical methods are generally not applied
to the production of metallic powders.

Mechanical activation has been used for the production of
25 fine powders with particle sizes typically in the range of
0.2 to 2 microns. One method for the production of powders
by mechanical activation is the process of mechanical
alloying described in U.S. Patent No. 3,591,362, by which
alloys are formed from pure starting materials by milling a
30 mixture of the powders in a high energy ball mill. During
milling the constituent particles undergo repeated collisions
with the grinding balls causing deformation, welding and
fracture of the particles which result in microstructural
refinement and composition changes leading to the formation

- 2 -

of nanocrystalline or amorphous alloys.

Another example of the use of mechanical activation to form fine powders, as described in U.S. Patent 5,328,501, is concerned with a mechanochemical reduction process. This process involves the mechanically activated chemical reduction of reducible metal compounds with a reductant during milling in a high energy ball mill, to refine and manufacture metals, alloys and composite powders. During milling the energy imparted to the reactants through ball/reactant collision events causes repeated welding and fracture of the reactant particles. Consequently oxidation/reduction reactions occur at welded interfaces and reaction kinetics are enhanced without the need for high temperatures or melting to increase intrinsic reaction rates.

With both the above described prior art mechanically activated processes micron sized particles are formed which contain a nanometre scale mixture of phases, crystallites or amorphous regions. These processes have not previously been known to result in powders containing a significant fraction of particles with sizes less than 50nm or interconnected networks of ultrafine particles exhibiting high values of specific surface area.

SUMMARY OF THE INVENTION

The present invention is concerned with a new process for the manufacture of ultrafine particles which is based on mechanically activated chemical reaction of a metal compound with a suitable reagent.

The process of the invention is based on the discovery that mechanical activation can be used to provide an improved, cost effective process for the production of ultrafine particles.

According to one aspect of the present invention there is

- 3 -

provided a process for the production of ultrafine particles, the process comprising:

subjecting a mixture of a metal compound and a suitable reagent to mechanical activation to increase the chemical
5   reactivity of the reactants and/or reaction kinetics such that a chemical reaction can occur which produces a solid nanophase substance and concomitantly forms a by-product phase; and,

removing the by-product phase such that the solid nanophase
10   substance is left behind in the form of ultrafine particles.

The term "ultrafine particles" as used above and throughout the remainder of the specification refers to individual particles in powder form as well as to particles interconnected or embedded in a porous matrix, and typically
15   includes nano particles in the size range of 1 nm to 200 nm, or more typically in the range 5 nm to 50 nm.

During mechanical activation a composite structure is typically formed which consists of an intimate mixture of nano-sized grains of the nanophase substance and the reaction
20   by-product phase. The step of removing the by-product phase, following mechanical activation, may involve subjecting the composite structure to a suitable solvent which dissolves the by-product phase, while not reacting with the solid nanophase substance. Removal of the by-product leaves behind ultrafine
25   particles of the solid nanophase substance. Alternatively, the composite structure may be subjected to heating to remove the by-product phase by evaporation. If necessary, the surfaces of the ultrafine particles may be further processed (e.g. by gaseous reduction) to remove oxide or passivating
30   films formed during removal of the by-product phase.

In one form of the process of the invention the metal compound is an unreduc d metal compound and the reagent is a

- 4 -

suitable reductant so that when the mixture is subjected to mechanical activation a chemical reaction occurs which reduces the metal compound to a metal phase, so that subsequent removal of the by-product phase leaves behind the

5   metal phase in the form of ultrafine particles.

Preferably the unreduced metal compound is selected from the group containing metals of low electro-negativity, including but not limited to iron, nickel, cobalt, copper, gold and platinum. Typically the unreduced metal compound is a metal

10   oxide, a metal chloride or a metal sulphide.

Preferably the reductant is a reducing agent which forms a soluble by-product phase. Examples of suitable reductants include sodium, calcium, magnesium and aluminium.

In one embodiment of the process the mixture formed during

15   mechanical activation consists of nanocrystallites of the metal phase embedded within the reaction by-product phase, such that the metal phase does not percolate through the particles. Removal of the by-product phase leaves a powder consisting of nanoparticles of the metal phase.

20   In a second embodiment of the process, the nanocrystallites of the metal phase formed by mechanical activation are percolated or interconnected through the by-product phase. Removal of the reaction by-product phase then results in micron sized particles of the metal phase interconnected in

25   a sponge-like structure.

In another form of the process of the invention mechanical activation results in an increase in the chemical reactivity of the reactants and/or reaction kinetics such that a displacement reaction can occur which produces a non-metallic

30   phase such as a ceramic compound, so that subsequent removal of the by-product phase leaves behind the non-metallic phase in the form of ultrafine particles.

- 5 -

With some reactants the displacement reaction may not occur until the mixture is subject to thermal treatment, such as by annealing, either simultaneous with or subsequent to mechanical activation.

5   The process may be applied to the formation of single phase alloy particles, including solid solutions and intermetallics, metal oxide or sulphide particles.

The process may be applied to the formation of nano-sized powders consisting of a mixture of two types of particles

10   each of a different phase.

The process may be applied to the manufacture of nano particles of oxides, carbides or other compounds by subsequent reaction of the metal particles with gaseous or liquid reactants to form the required phase.

15   The process may also utilise heat treatment of the powder following mechanical activation and prior to removal of the reaction by-product to form a desired phase or optimise morphology for particular applications.

The process may be applied to the formation of nano particles

20   which are embedded in a porous matrix. The porous matrix may be a reaction by-product phase formed mechanochemically and not removed or may be a third phase which remains after removal of a soluble by-product phase.

In a preferred form of the invention, mechanical activation

25   is performed inside a mechanical mill, for example, a ball mill. Mechanical activation occurs in a ball mill when grinding media, typically steel or ceramic balls, are kept in a state of continuous relative motion with a feed material by the application of mechanical energy, such that the energy

30   imparted to the feed material during ball-feed-ball and ball-feed-liner collisions is sufficient to cause mechanical

- 6 -

activation.

Throughout the remainder of the specification reference will be made to mechanical activation being carried out inside a mechanical mill. Examples of this type of mill are attritor mills, nutating mills, tower mills, planetary mills, vibratory mills and gravity-dependent-type ball mills.

It will be appreciated that the mechanical activation may also be achieved by any suitable means other than ball milling. For example, mechanical activation may also be achieved using jet mills, rod mills, roller mills or crusher mills.

The roles of mechanical activation in relation to the synthesis of ultrafine particles are :

(i)   to develop a nanoscale mixture of the two reactants;

(ii)   to cause a chemical reaction between the reactants during mechanical activation which enables the product phases to form a nanoscale mixture containing separated nano-sized particles of the product phase; and

(iii)   if the chemical reaction does not occur during mechanical activation, to increase the chemical reactivity and/or reaction kinetics of any subsequent reactions which occur on heating such that the reaction temperature is lower than the temperature normally needed for grain growth or particle coarsening.

Important factors determining the morphology of the product phase are the volume fraction of the by-product phase formed during milling, and milling parameters including the collision energy and ball size. The volume fraction of the by-product phase is a function of the reaction stoichiometry and the densities of the product phases. In the case of reduction/oxidation reactions, the highest volume fraction of the by-product phase is associated with metal compounds of

- 7 -

the highest valency and reductants having the lowest valence.
There is a minimum volume fraction of the by-product phase
necessary for the desired phase to form in discrete particles
during the reaction. If the volume fraction of the by-
5   product phase is insufficient for separated particles of the
desired phase to form during milling, powders of the by-
product phase or other inert phases may be added prior to
milling and milled with the reacting phases. Alternatively,
if an interconnected product phase is required, the volume
10 fraction of the by-product phase should be less than a
critical value. If the desired phase is a metal the volume
fraction of the by-product phase may be minimised by choosing
reducible compounds of low valency and reductants of high
valency.

15 The particle size formed during milling can also be a
function of the type of milling process employed, the ball
size and milling time. Of particular importance is the
collision energy associated with ball/powder collisions,
which is determined by the ball to powder mass ratio (charge
20 ratio) and the ball size and other parameters associated with
the particular milling process employed. As described in
U.S. Patent 5,328,501, if the collision energy during milling
is too high the exothermic nature of a chemical reduction
reaction can cause it to occur in an unstable, combustive
25 manner, resulting in melting and even vaporisation of the
product phases and a significant increase in particle size
and changes in product morphology. The collision energy
required to cause combustion is a function of the enthalpy
change associated with the reaction as well as other factors.

30 The processing parameters depend on the nature of the metal
compounds being processed, the size and distribution of the
ultrafine particles being produced and the type of mechanical
activation employed.

In the process of ball milling the reactants, including the

- 8 -

metal compound and a suitable reagent, collide with each other and the grinding media. Either the reagent or the metal compound will be a solid and the reactivity of the reactants increases due to the increase in reaction area
5   resulting from the decrease in the grain and particle sizes of the solid phase associated with collision events. A welding, mixing of atoms and/or exchange of atoms occurs at the interfaces of colliding particles to promote reactivity. With solid reagents a displacement reaction may occur at or
10   near the interfaces during the compaction and welding of the metal compound and the reagent. With liquid or gaseous reagents, the reaction may occur as a result of the contact of fresh surfaces of the metal compound created by the ball/powder collisions in the ball mill with the reagent
15   atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS
The invention is further described in and illustrated by the following examples, which are not to be construed as limiting the invention in any way, to be read in conjunction with the
20   accompanying drawings, in which:

Figure 1 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently washed mixture of $FeCl_3$ and Na;

Figure 2 is a TEM micrograph of Fe particles after washing;

25   Figure 3 is a graphical representation of magnetisation measurements taken after milling of the $FeCl_3$ and Na for various times;

Figure 4 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently washed mixture of
30   $CuCl_2$ and Na;

Figure 5 is a TEM micrograph of Cu particles after washing;

- 9 -

Figure 6 is a TEM micrograph of a porous structure of Cu nano particles;

Figure 7 is a TEM micrograph of Ni nano particles;

Figure 8 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently annealed mixture of $AlCl_3$ and CaO;

Figure 9 is a TEM micrograph of Al_2O_3 particles after washing; and,

Figure 10 is a TEM micrograph of ZrO_2 particles after washing.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

EXAMPLE 1 - Synthesis of Ultrafine Iron Particles

The materials used were anhydrous $FeCl_3$ powder (-100 mesh) and Na pieces ($\leq$ 5 mm). The starting mixture of $FeCl_3$ and Na in a molar ratio of 1:3, corresponding to the reaction:
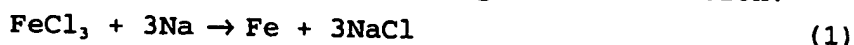
$$FeCl_3 + 3Na \rightarrow Fe + 3NaCl \qquad (1)$$

was loaded and sealed in a hardened steel vial with twenty 4.8mm steel balls under an argon atmosphere. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed several times with deionised, deoxygenated water and rinsed with methanol in an ultrasound cleaner. The washed powder was dried by evaporation and all subsequent powder handling was carried out in an argon filled glove box.

Fig. 1 shows the x-ray diffraction patterns of as-milled and subsequently washed powders milled for 8 hours. The as-milled powder consisted of a mixture of NaCl and Fe. The formation of Fe is due to the mechanically activated reduction of $FeCl_3$ by Na via the reaction (1) above during milling. No NaCl was visible in the x-ray diffraction patterns of the powder after the washing process (Fig. 1).

- 10 -

The peaks for the α-Fe phase were broad, corresponding to a crystallite size of approximately 10 nm. Residual unreacted $FeCl_3$ and Na were also removed during washing.

5 A TEM micrograph of the Fe particles after washing is shown in Fig. 2. Most of the Fe particles had a size of ~10nm and each particle consists of a single crystal or grain of Fe. No traces of chlorine or sodium were found using energy dispersive spectroscopy. The effective surface area of the iron particle measured by the BET method was 32 m^2/g.

10 The progress of the reaction was followed with measurements of magnetisation to determine the amount of iron present. Fig. 3 shows measurements of magnetisation as a function of milling time for samples milled with 4.8mm steel balls. To complete the formation of the Fe particles required a milling 15 time of approximately 6-8 hours using the SPEX 8000 mixer/mill. The particle size measured using x-ray diffraction and electron microscopy was about 10nm for milling times up to 8 hours. With increasing milling times, the particle size increased slowly to about 20 nm after 20 milling for 40 hours. Using a smaller ball size of 3.2 mm diameter, resulted in a decrease in the particle size to an average of 7 nm after 24 hours of milling.

When larger balls were used, (9.5 and 12 mm diameter) a combustion reaction was observed. The resulting Fe articles 25 could be classified into two groups. One group had a particle size around 10nm, similar to that obtained using smaller balls, while the other had a wide range of larger particle sizes of 60-200 nm. The larger particles were formed by vaporisation and condensation of Fe as a 30 consequence of the combustion reaction.

Fe particles were also produced by mechanochemical reduction of $FeCl_3$ using Mg and Al powders as the reducing agents, by the following chemical reactions:

- 11 -

the following chemical reactions:

$$FeCl_3 + 1.5Mg \rightarrow Fe + 1.5 \ MgCl_2 \qquad (2)$$

$$FeCl_3 + Al \rightarrow Fe + AlCl_3 \qquad (3)$$
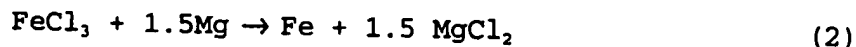
The milling conditions used were the same as for reaction (1) described above.

Reactions (2) and (3) differ from reaction (1) by the molar ratio of the iron to the chloride reaction by-product. Table 1 shows the particle size produced after milling and molar ratio of Fe to chloride for each reaction. It will be seen that there is a correlation between the respective particle sizes and the molar ratios, with the particle size increasing with increasing molar ratio. It is noted that for a given reaction the molar ratio may be decreased by adding additional reaction by-product to the reactants prior to milling.

TABLE 1

Reaction	Particle Size	Molar Ratio
$FeCl_3 + 3Na \rightarrow Fe + 3NaCl$	10 nm	0.33
$FeCl_3 + 1.5Mg \rightarrow Fe + 1.5MgCl_2$	40 - 100 nm	0.66
$FeCl_3 + Al \rightarrow Fe + AlCl_3$	3 - 10 μm	1.00

Ultrafine Fe particles have also been successfully prepared using an attritor, where the particle size was similar to that prepared using SPEX 8000 mixer/mill.

EXAMPLE 2 - Synthesis of Ultrafine Copper Particles

The materials used were anhydrous $CuCl_2$ powder (-100 mesh) and Na pieces (55mm), Mg powder (-100 mesh) or Al powder (-100 mesh). Mixtures of the reactants corresponding to the reactions:
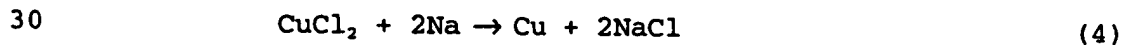
$$CuCl_2 + 2Na \rightarrow Cu + 2NaCl \qquad (4)$$

$$CuCl_2 + Mg \rightarrow Cu + MgCl_2 \qquad (5)$$

$$3CuCl_2 + 2Fe \rightarrow 3Cu + 2FeCl_3 \qquad (6)$$

were loaded and sealed in a hardened steel vial with twenty 4.8mm steel balls under an argon atmosphere. The mechanical

- 12 -

as-milled powder was washed several times with deionised, deoxygenated water and rinsed with methanol in an ultrasound cleaner. The washed powder was dried by evaporation and all subsequent powder handling was carried out in an argon filled

5   glove box.

Fig. 4 shows the x-ray diffraction patterns for powders from reaction (4) after milling for 8 hours and after washing. The as-milled powder consisted of a mixture of NaCl and Cu. The formation of Cu is due to the reduction of $CuCl_2$ via

10 reaction (4) above during milling. No NaCl was visible in the x-ray diffraction patterns of the powder after the washing process (Fig. 4). The peaks for the Cu phase were broad, corresponding to an average crystallite size of approximately 20 nm.

15 A TEM micrograph of the Cu particles after washing is shown in Fig. 5. The Cu particles have sizes of ~20-100 nm and each particle consists of a single crystal or grain of Cu.

Reactions (5) and (6) differ from reaction (4) by the molar ratio of the copper to the chloride reaction by-product.

20 Table 2 shows the particle sizes produced after milling and volume ratio of copper to chloride for each reaction. It is seen that results show an excellent correlation between the particle size and the molar ratios.

TABLE 2

25 | Reaction | Particle Size | Molar Ratio |
|---|---|---|
| $CuCl_3$ + 2Na → Cu + 2NaCl | 10 - 100 nm | 0.5 |
| $CuCl_3$ + Mg → Cu + $MgCl_2$ | 30 - 300 nm | 1.0 |
| $3CuCl_3$ + 2Fe → 3Cu + $2FeCl_3$ | 0.1 - 20 μm | 1.5 |

30 Cu particles synthesised from reaction (6) exhibited a wide size distribution of 0.1-20μm. A typical particle is shown in Figure 6. The particles had a porous structure, where

- 13 -

each particle consisted of composite of many small interconnected Cu particles, indicating that the low volume fraction of $FeCl_3$ was insufficient to separate the individual Cu particles.

5   **EXAMPLE 3 - Synthesis of Ultrafine Nickel Particles**
Ni particles were synthesised through the reaction of $NiCl_2$ + $2Na \rightarrow Ni + 2NaCl$ using the milling and other conditions described in Example 1. The resulting particle sizes as determined from x-ray diffraction and transmission electron
10   microscopy measurement were in the range of 10 to 20nm. Fig. 7 shows typical nano particles of nickel produced by the reaction.

EXAMPLE 4 - Synthesis of Ultrafine Cobalt Particles
Co particles were synthesised through the reaction of $CoCl_2$
15   + $2Na \rightarrow Co + 2NaCl$ using the milling and other conditions described in Example 1. The resulting particle sizes as determined from x-ray diffraction and transmission electron microscopy measurement were in the range of 20 to 50nm. The particle sizes were almost identical to that for the nickel
20   as expected since these two reactions have the same molar by-product ratio.

EXAMPLE 5 - Synthesis of Fe-Ni Alloy Particles
Particles of an iron-nickel were synthesised by the reaction of $FeCl_3$ + $NiCl_2$ + $5Na \rightarrow FeNi + 5NaCl$ using the milling and
25   other conditions described in Example 1. X-ray diffraction showed that the powder consisted of an fcc phase, indicating the formation of the alloy of $Fe_{50}Ni_{50}$. This composition was confirmed by a Fe^{57} - Mössbauer study. The particle size was 5-10nm.

30   All of the above examples involved mechanical activation of an unreduced metal compound and a suitable reductant such that an oxidation/ reduction reaction occurred to form ultrafine metal powders. However it has been found that the

- 14 -

process of the invention can also be applied to the production of other ultrafine powders using reactions which do not involve oxidation or reduction of the reactants.

5 For example the following reactions for making ultrafine ceramic powders (Al_2O_3 - alumina, ZrO_2 - zirconia) may also be employed:
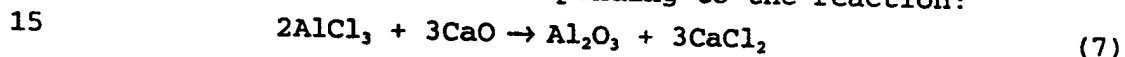
$$2AlCl_3 + 3CaO \rightarrow Al_2O_3 + 3CaCl_2$$
$$2Al(OH)_3 + 3CaO \rightarrow Al_2O_3 + 3Ca(OH)_2$$
$$ZrCl_4 + 2CaO \rightarrow ZrO_2 + 2CaCl_2$$
10
$$2AlCl_3 + 3Ca(OH)_2 \rightarrow Al_2O_3 + 3CaCl_2 + 3H_2O$$
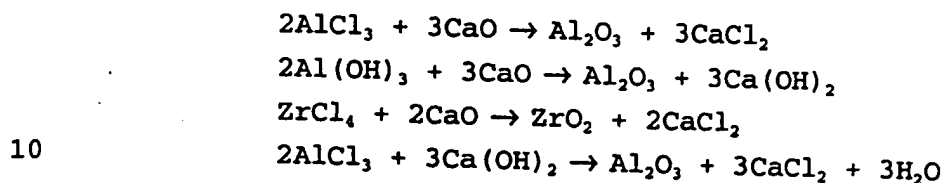
EXAMPLE 6 - Synthesis of Ultrafine Alumina Particles

The materials used were anhydrous AlC13 (≤100 mesh) and CaO (≤100 mesh). The starting mixture of $AlCl_3$ and CaO in a molar ratio of 2:3, corresponding to the reaction:

15
$$2AlCl_3 + 3CaO \rightarrow Al_2O_3 + 3CaCl_2 \tag{7}$$

was loaded and sealed in a hardened steel vial with 9.5mm steel balls under an air atmosphere. The ball to powder mass ratio was 8.1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. Figure 8 shows an x-ray

20 diffraction pattern of the as-milled powder. Only the diffraction peaks of CaO phase were present on the XRD patterns of as-milled samples. TEM examination showed micron sized particles consisting of an agglomeration of nanocrystallites of CaO embedded in an amorphous matrix. No

25 evidence of the formation of Al_2O_3 was found after milling. XRD diffraction patterns for samples heated to 150°, 300° and 400°C are also shown in Figure 8. The patterns show that heating at 150°C caused formation of the $AlCaCl_5$ phase, due to the reaction $5AlCl_3 + 3CaO \rightarrow 3AlCaCl_5 + Al_2O_3$. X-ray

30 diffraction measurements on samples annealed at 300°C showed peaks associated with $CaCl_2$ and a reduction in intensity of the $AlCaCl_5$ and CaO peaks, thus indicating that the reaction $AlCaCl_5 + CaO \rightarrow Al_2O_3 + CaCl_2$ occurred. Completion of the formation of $CaCl_2$ required an annealing temperature of 350°C

35 or above. All peaks in the x-ray diffraction pattern of the

sample annealed at 400°C could be indexed to the $CaCl_2$ phase. No crystalline alumina phases were seen in the XRD patterns of samples annealed at 350° and 400°C, however, this was due to the small fraction of alumina present and the small particle size.

Figure 9 shows a transmission electron micrograph of a sample milled for 24 hours, heat treated at 350°C and washed in water to remove the $CaCl_2$ reaction by-product. The sample consisted of individual particles of alumina with sizes between 10 and 20nm. The sample formed α - Al_2O_3 after heat treatment at 1250°C. Similar results were obtained in samples milled with 6.4 and 12.6mm balls.

Example 7 Synthesis of Ultrafine Zirconia Particles

The materials used were anhydrous $ZrCl_4$ (^{2}100 mesh) and CaO (^{2}100 mesh). The starting mixture of $ZrCl_4$ and CaO in a molar ratio of 1:2, corresponding to the reaction:

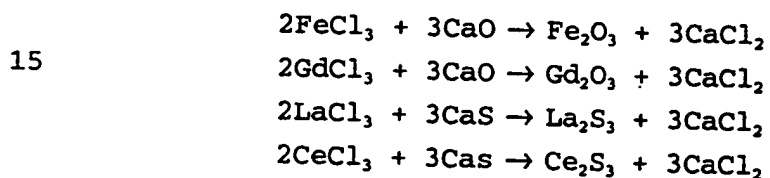$$ZrCl_4 + 2CaO \rightarrow ZrO_2 + 2CaCl_2 \qquad (8)$$

was loaded and sealed in a hardened steel vial with 12 mm diameter steel balls under an air atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. X-ray diffraction analysis of the as-milled powder showed only the presence of CaO. No evidence of the formation of ZrO_2 was found after milling user x-ray diffraction measurements. Transmission electron microscopy examination showed micron sized particles consisting of an agglomeration of nanocrystallites of CaO embedded in an amorphous matrix.

Formation of ZrO_2 nanoparticles occurred during heat treatment at 400°C. Figure 10 shows a transmission electron micrograph of a sample milled for 24 hours, heat treated at 400°C and washed in water to remove the $CaCl_2$ reaction by-product. The sample consisted of individual particles of zirconia with sizes between 5 and 20nm.

- 16 -

These examples show that the production of nano-sized alumina and zirconia particles by mechanochemical processing can be achieved from economical starting materials - $AlCl_3$, $ZrCl_4$ and CaO. The process includes a milling at a relatively low energy level, annealing at 300-400°C and a simple washing process. Milling at low energy level is promising for large quantity production using commercial mills. Therefore, the development of this processing method may lead to a new production process of nano-sized alumina and other ceramic powders in an economical and efficient way.

Examples of other reactions in accordance with the invention which do not involve oxidation or reduction of the reactants to produce ultrafine particles are:

$$2FeCl_3 + 3CaO \rightarrow Fe_2O_3 + 3CaCl_2$$
$$2GdCl_3 + 3CaO \rightarrow Gd_2O_3 + 3CaCl_2$$
$$2LaCl_3 + 3CaS \rightarrow La_2S_3 + 3CaCl_2$$
$$2CeCl_3 + 3CaS \rightarrow Ce_2S_3 + 3CaCl_2$$

EXAMPLE 8

Ultrafine hematite Fe_2O_3 powders have been synthesized by mechanochemical processing based on the solid-state reactions;

$$2FeCl_3 + 3CaO \rightarrow Fe_2O_3 + 3CaCl_2$$
$$2FeCl_3 + 3Ca(OH)_2 \rightarrow Fe_2O_3 + 3CaCl_2 + 3H_2O.$$
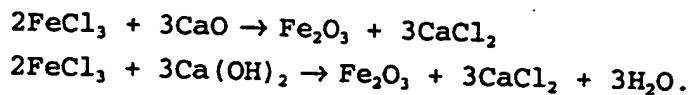
Dried $FeCl_3$, $CaCl_2$, CaO and $Ca(OH)_2$ powders of >99% purity were used as the starting materials. Mechanical milling was carried out for 24 hours in a sealed, hardened steel vial using a SPEX 8000 mixer/mill. The charge ratio of ball to powder mass was 5:1 and 4.8mm diameter hardened steel balls were used. Initial powder handling and vial loading were carried out in a high-purity argon filled glove box. After milling, the powders were heat treated in a vacuum at temperatures b tween 50 and 600°C for 60 minutes. To remove the reaction by-product, the samples were washed with methanol in an ultrasound bath and dried.

- 17 -

Milling of $2FeCl_3$ + $3CaO$ led to a nanocrystalline mixture of these two compounds. Fe_2O_3 was formed after annealing at 150°C or above. After washing the powder mainly consisted of single crystal Fe_2O_3 platelets, with a particle size distribution in the range of 100-500nm. An addition of 100% $CaCl_2$, ie. $2FeCl_3$ + $3CaO$ + $5CaCl_2$, into the starting material resulted in a strong reduction of the Fe_2O_3 particle size to 10-30nm.

Nanocrystalline tetragonal akaganeite, FeOOH phase, together with calcium chloride was found after milling of $2FeCl_3$ + $3Ca(OH)_2$. Fe_2O_3 was formed after dehydration through heat treatment at temperatures above 200°C. Pure ultrafine Fe_2O_3 particles of 20-50nm in size were obtained after a washing process using methanol to remove the $CaCl_2$ reaction by-product.

**EXAMPLE 9 - Synthesis of Ultrafine Rare Earth Oxide Particles**
The reaction of $2GdCl_3$ + $3CaO \rightarrow Gd_2O_3$ + $3CaCl_2$ has a negative free energy of about 70 KJ/mole. The materials used were anhydrous $GdCl_3$ (-20 mesh) and CaO ($\leq$-100 mesh). The starting mixture of $GdCl_3$ and CaO in a molar ratio of 2:3 was loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed in the same manner as in Example 1.

After milling for 24 hours, GdOCl was formed due to the reaction of $GdCl_3$ + $CaO \rightarrow GdOCl$ + $2CaCl_2$. The particle size of GdOCl as determined from transmission electron microscopy measurements was 10 - 50nm. The formation of Gd_2O_3 ultrafine particles occurred during the heat treatment of the milled sample at 700°C or above. The resulting particle size was approximately 100nm.

- 18 -

EXAMPLE 10 - Synthesis of Ultrafine Rare Earth Sulfide Particles

The materials used were anhydrous rare earth chlorides such as $LaCl_3$ and $CeCl_3$ (-20 mesh), and CaS ($\leq$-100 mesh). The starting mixture of rare earth chloride and CaS in a molar ratio of 2:3, corresponding to the reactions:
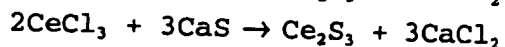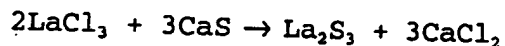
$$2LaCl_3 + 3CaS \rightarrow La_2S_3 + 3CaCl_2$$
$$2CeCl_3 + 3CaS \rightarrow Ce_2S_3 + 3CaCl_2$$

were loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. The as-milled powder was washed several times with methanol in an ultrasound cleaner. The resulting particle sizes as determined from X-ray diffraction and transmission electron microscopy measurements were in the range of 10 to 100nm.

EXAMPLE 11 - Synthesis of Ultrafine Zinc Sulfide Particles

The materials used were anhydrous $ZnCl_2$ (-20 mesh) and CaS ($\leq$-100 mesh and ~10nm). The starting mixture of $ZnCl_2$ and CaS in a molar ratio of 1:1 corresponding to the reaction $ZnCl_2 + CaS \rightarrow ZnS + CaCl_2$ was loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed several times with methanol in an ultrasound cleaner. Using CaS of $\leq$-100 mesh, the complete formation of ZnS particles required a milling time of approximately 36 hours. The resulting particle size as determined from X-ray diffraction and transmission electron microscopy measurements was approximately 15nm. On the other hand, with CaS of ~10nm, which was synthesised by mechanical alloying, the resulting particle size was 5 - 10nm.

The process for the production of ultrafine particles using

- 19 -

mechanical activation as described above, has a number of advantages over conventional processing methods including:

(1)   The process is essentially a low temperature process and therefore does not require the complex control systems associated with some chemical and physical production methods.

(2)   The process enables a significant degree of control over the size and size distribution of the ultrafine particles production by controlling the parameters of mechanical activation and the reaction stoichiometry.

(3)   The process also enables a significant degree of control over the nature of interfaces created between the solid nanophase substance and the reaction by-product phase.

(4)   The process is relatively inexpensive and has a high yield rate, so that it can be readily modified for the synthesis of ultrafine particles on a commercial scale.

It will be apparent to persons skilled in the materials and chemical engineering arts that numerous enhancements and modifications can be made to the above described process without departing from the basic inventive concepts. All such modifications and enhancements are considered to be within the scope of the present invention, the nature of which is to be determined from the foregoing description. Furthermore, the preceding examples are provided for illustrative purposes only, and are not intended to limit the scope of the process of the invention.

- 20 -

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.   A process for the production of ultrafine
particles, the process comprising:

subjecting a mixture of a metal compound and a suitable
5   reagent to mechanical activation to increase the chemical
reactivity of the reactants and/or reaction kinetics such
that a chemical reaction can occur which produces a solid
nanophase substance and concomitantly forms a by-product
phase; and,

10   removing the by-product phase such that the solid nanophase
substance is left behind in the form of ultrafine particles.

2.   A process for the production of ultrafine particles
as defined in claim 1, wherein said solid nanophase substance
includes nano particles in the size range of 1nm to 200nm.

15   3.   A process for the production of ultrafine particles
as defined in claim 2, wherein said solid nanophase substance
includes nano particles in the size range of 5nm to 50nm.

4.   A process for the production of ultrafine particles
as defined in claim 1, wherein during mechanical activation
20   a composite structure is typically formed which consists of
an intimate mixture of nano-sized grains of the nanophase
substance and the reaction by-product phase.

5.   A process for the production of ultrafine particles
as defined in claim 4, wherein the step of removing the by-
25   product phase, following mechanical activation, involves
subjecting the composite structure to a suitable solvent
which dissolves the by-product phase, while not reacting with
the solid nanophase substance.

6.   A process for the production of ultrafine particles

as defined in claim 4, wherein the composite structure is subjected to heating to remove the by-product phase by evaporation.

7.   A process for the production of ultrafine particles as defined in claim 1, further comprising the step of further processing the surfaces of the ultrafine particles to remove oxide or passivating films formed during removal of the by-product phase.

8.   A process for the production of ultrafine particles as defined in claim 1, wherein the metal compound is an unreduced metal compound and the reagent is a suitable reductant so that when the mixture is subjected to mechanical activation a chemical reaction occurs which reduces the metal compound to a metal phase, so that subsequent removal of the by-product phase leaves behind the metal phase in the form of ultrafine particles.

9.   A process for the production of ultrafine particles as defined in claim 8, wherein the unreduced metal compound is selected from the group containing metals of low electro-negativity, including but not limited to iron, nickel, cobalt, copper, gold and platinum.

10.   A process for the production of ultrafine particles as defined in claim 9, wherein the unreduced metal compound is selected from the group consisting of metal oxides, metal chlorides and metal sulphides.

11.   A process for the production of ultrafine particles as defined in claim 8, wherein the reductant is a reducing agent which forms a soluble by-product phase, including the reducing agents sodium, calcium, magnesium and aluminium.

12.   A process for the production of ultrafine particles as defined in claim 8, wherein the mixture formed during

- 22 -

mechanical activation consists of nanocrystallites of the metal phase embedded within the reaction by-product phase, such that the metal phase does not percolate through the particles, and wherein removal of the by-product phase leaves
5   a powder consisting of nanoparticles of the metal phase.

13.   A process for the production of ultrafine particles as defined in claim 8, wherein the mixture formed during mechanical activation consists of nanocrystallites of the metal phase embedded within the by-product phase, such that
10   the nanocrystallites of the metal phase formed by mechanical activation are percolated or interconnected through the by-product phase, and wherein

removal of the reaction by-product phase then results in micron sized particles of the metal phase interconnected in
15   a sponge-like structure.

14.   A process for the production of ultrafine particles as defined in claim 1, wherein mechanical activation results in an increase in the chemical reactivity of the reactants and/or reaction kinetics such that a displacement reaction
20   can occur which produces a non-metallic phase such as a ceramic compound, so that subsequent removal of the by-product phase leaves behind the non-metallic phase in the form of ultrafine particles.

15.   A process for the production of ultrafine particles
25   as defined in claim 14, further comprising subjecting the mixture to thermal treatment, such as by annealing, either simultaneous with or subsequent to mechanical activation to enable the displacement reaction to occur.

Figure 1
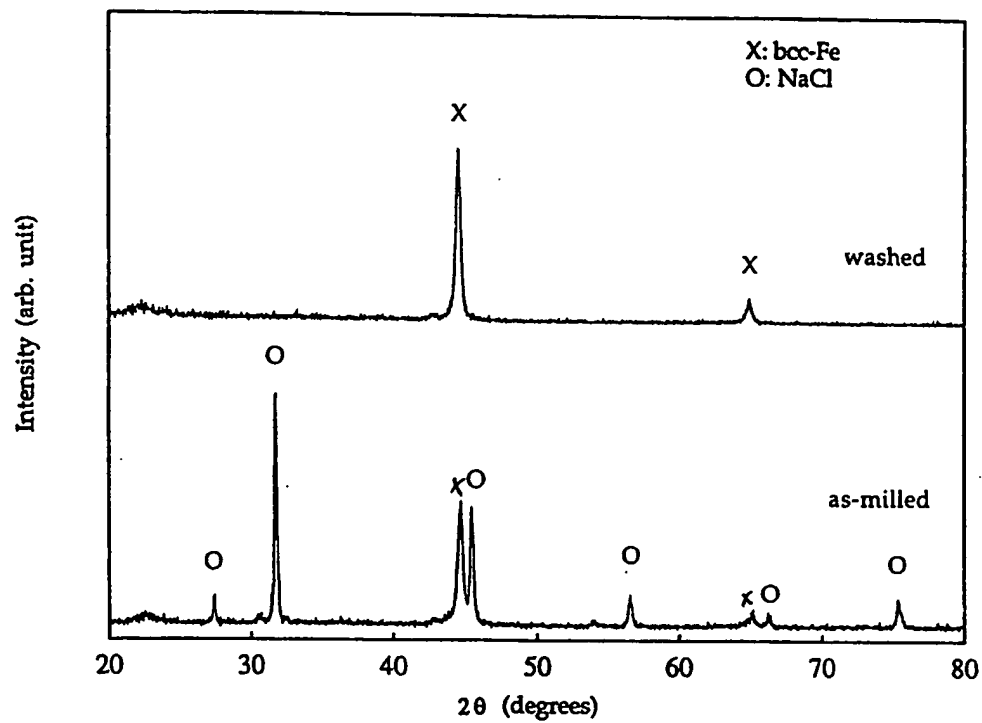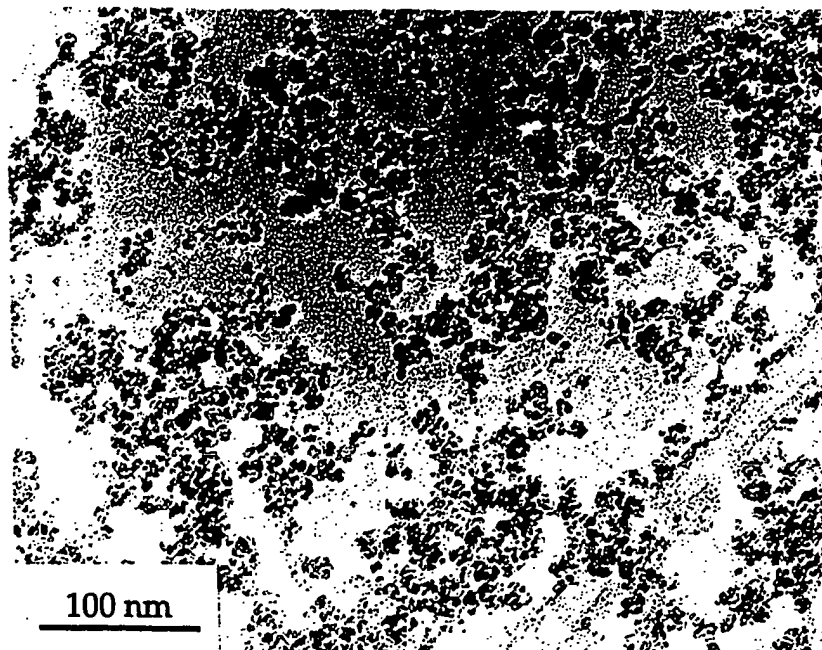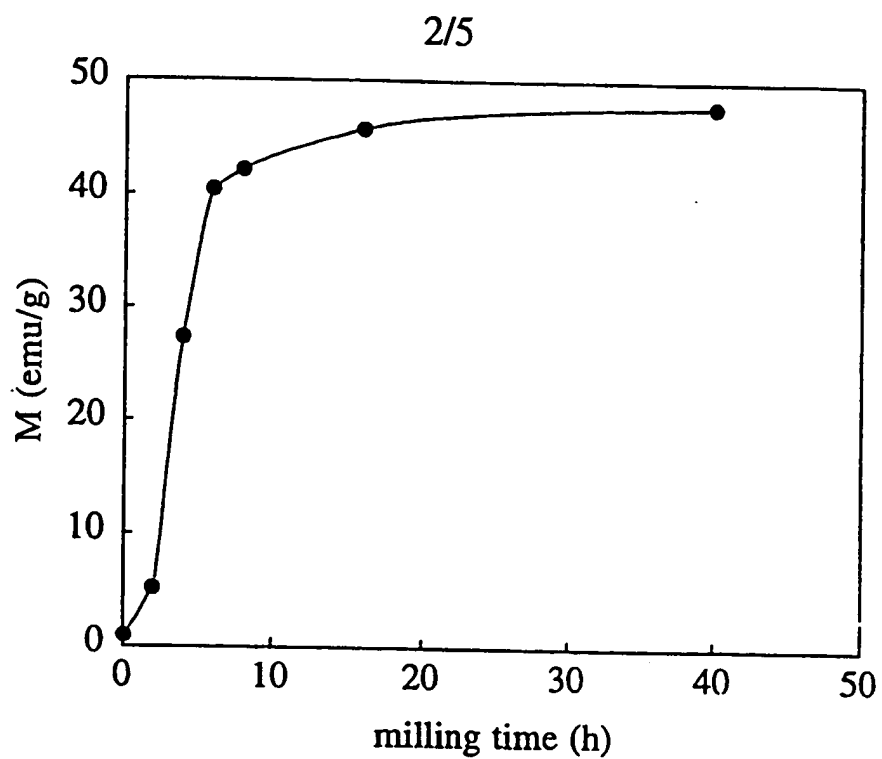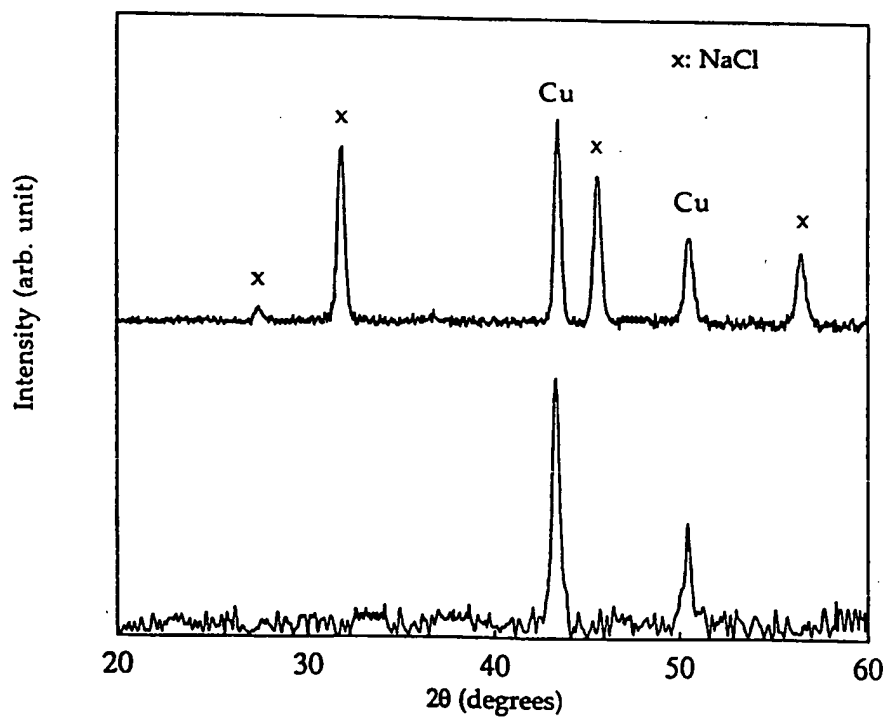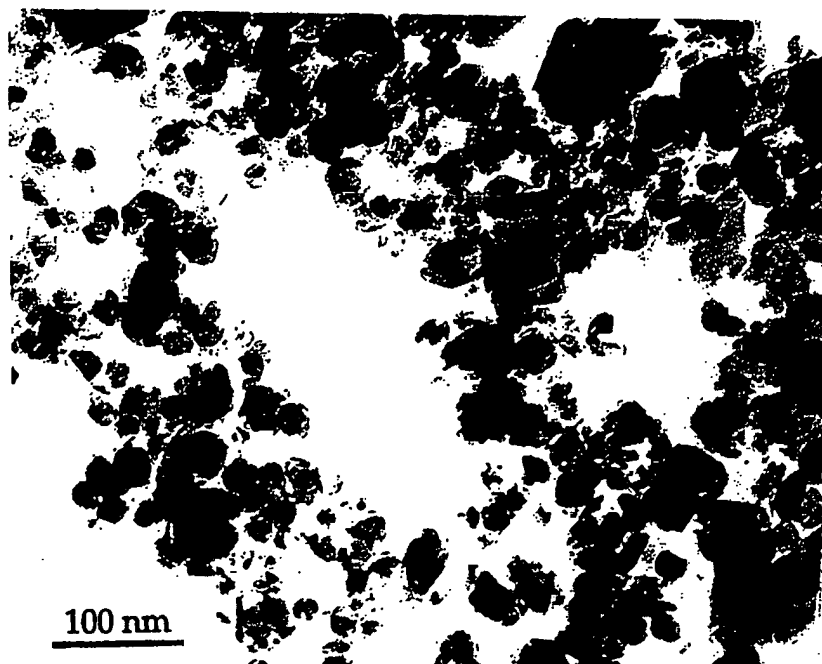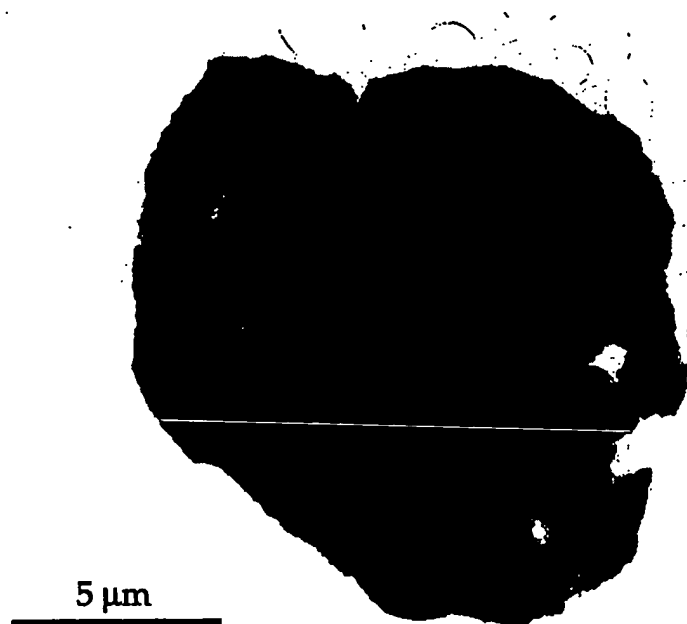

Figure 2

2/5

Figure 3

Figure 4

100 nm

Figure 5

5 μm

Figure 6

4/5

Figure 7
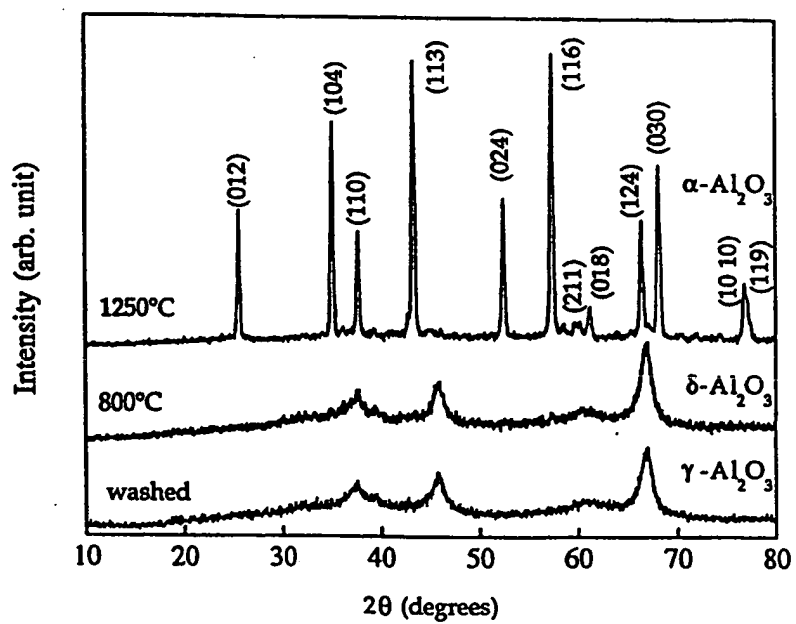
Figure 8

50 nm
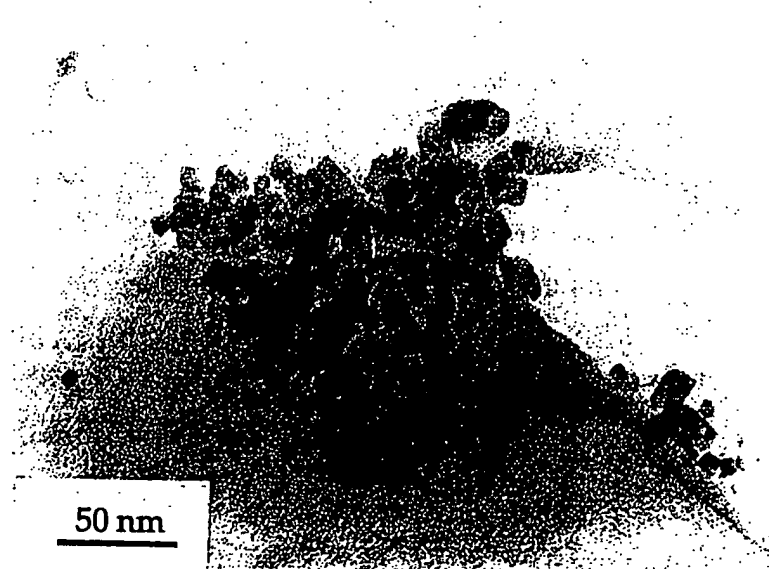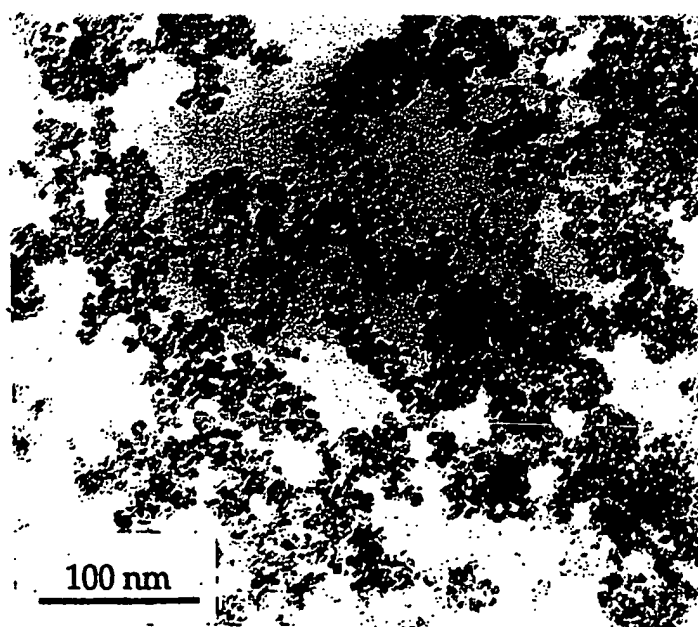
Figure 9

100 nm

Figure 10

A.	CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: B22F 9/16, 9/20; C22B 5/02, 5/04, 15/00, 23/02; C22C 1/04, 33/02, 38/08; C01F 7/02, 17/00; C01G 9/08, 25/02, 49/06; C04B 35/10, 35/48, 35/50, 35/622, 35/626

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
    B22F, C22B, C22C, C01F, C01G, C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT:[COMMINUT: OR REDUC: OR GRIND: OR MILL: OR MECHANIC: OR CRUSH: OR MIX:] AND [NANO: OR ULTRAFINE OR SUPERFINE OR ULTRA(W) FINE OR MICRO(W) FINE OR SUPER(W) FINE] AND IPC as above. JAPIO: [as above for WPAT] and [PHASE: OR REACT:]

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	AU 37681/95 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 17 May 1996 page 4 examples 1-3	1-5, 8-12
X	AU 76892/94 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 23 March 1995 page 4 lines 18-30 claims 1, 2, 13	1-5, 8-12
X	AU 48345/90 A (THE UNIVERSITY OF WESTERN AUSTRALIA) 28 June 1990 example 5 (procedure 1)	1, 2, 4, 5, 8-12

X	Further documents are listed in the continuation of Box C		X	See patent family annex

*	Special categories of cited documents:

"A"   document defining the general state of the art which is not considered to be of particular relevance

"E"   earlier document but published on or after the international filing date

"L"   document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O"   document referring to an oral disclosure, use, exhibition or other means

"P"   document published prior to the international filing date but later than the priority date claimed

"T"   later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"   document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"   document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"   document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 October 1996	15 OCT 1996

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929	N L KING Telephone No.: (06) 283 2150

INTERNATIONAL SEARCH REPORT

C (Continuation)   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	AU 36005/95 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 11 April 1996 entire document	1-15
P,A	AU 36004/95 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 11 April 1996 entire document	1-15
P,A	AU 37685/95 A (THE UNIVERSITY OF WESTERN AUSTRALIA) 23 May 1996 entire document	1-15
A	AU 13208/92 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 3 September 1992 entire document	1-15
A	AU 79677/91 A (THE AUSTRALIAN NATIONAL UNIVERSITY) 26 December 1991 entire document	1-15
A	US 5417956 A (MOSER) 23 May 1995 entire document	1-15
A	JP 57-145031 A (ONAHAMA SAKAI KAGAKU K.K.) 16 September 1981 abstract	1-15

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	37681/95	WO	9614268				
AU	76892/94	WO	9508004	EP	719346	CA	2169947
		ZA	9407050				
AU	48345/90	AU	627822	CA	2006402	DE	68925734
		AT	134389	EP	449890	IL	92832
		JP	4502490	NO	912406	NZ	231941
		US	5328501	WO	9007012	ZA	8909850
AU	36005/95	WO	9610653				
AU	36004/95	WO	9610539				
AU	37685/95	WO	9615279				
AU	13208/92	AU	645897	CA	2084085	EP	535055
		EP	574440	JP	6500601	JP	6507369
		US	5368812	US	5466310	WO	9119584
		WO	9214568				
AU	79677/91	AU	639803	CA	2084085	EP	535055
		EP	574440	JP	6500601	JP	6507369
		US	5368812	US	5466310	WO	9119584
		WO	9214568				
US	5417956	EP	655984	JP	8500289	WO	9404459

END OF ANNEX